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Effects of Nitrogen Oxides on Vegetation

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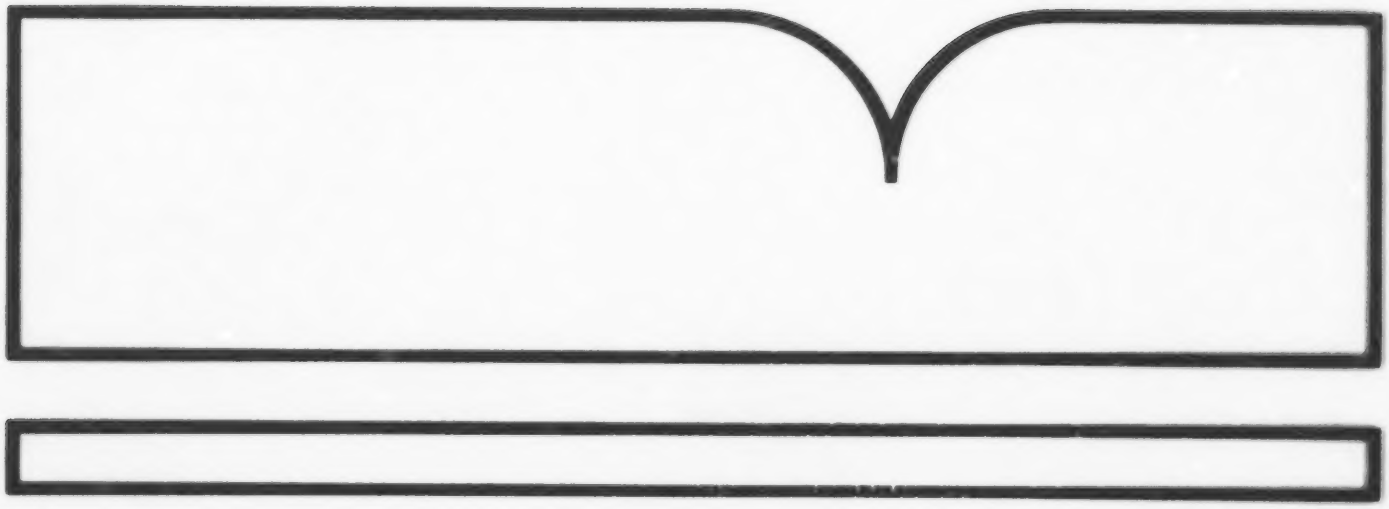

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EFFECTS OF NITROGEN OXIDES ON VEGETATION

by

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The data support the conclusion that lower plants are relatively tolerant of NO_2, as are higher plants. Gas-phase concentrations required to cause effects are much higher than occur in the ambient. However, caution must be exercised concerning the possible effects of nitrate and nitrite delivered to the plants via wet deposition processes as thallophytes can absorb the ions directly from the environment. Nitrite (0.5 to 1.0 mM) can reduce the chlorophyll content of lichens and the photosynthetic rate of algae. Additional studies are required to determine if the wet deposition rates that occur in ambient conditions are detrimental to lower plants.

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CHAPTER 1

EFFECTS OF NITROGEN OXIDES ON VEGETATION

1.1 Mode of Action

Vegetation responses to nitrogen oxides occur at various levels of biological organization ranging from the subcellular to the ecosystem. These various responses result from perturbations occurring at the subcellular level of organization and are initiated by changes in one or more biochemical and physiological processes. As has been shown for ozone (Tingey and Taylor, 1982), the initial biochemical and physiological events are controlled by processes involved with pollutant uptake and its metabolism. Pollutant uptake includes the diffusion of the pollutant from the ambient air into the cellular perturbation sites within the cells and includes both gas phase and liquid phase transfer processes. In the liquid phase, NO_2 dismutates to form nitrate and nitrite. The inital phytotoxic event (perturbation) results from alterations in subcellular structure or function induced by the pollutant. Following the perturbation, the plant may initiate homeostatic (recovery or compensatory) processes. Injury is the result of pollutant absorption and its subsequent reaction at active sites within the cell and is the consequence of the cell's inability to repair or compensate for dysfunctions.

1.1.1 NOx Deposition

The deposition of nitrogen oxides onto an ecosystem, plant community or individual plant may occur via either dry or wet (including occult) deposition

(Fowler, 1980; Dollard et al., 1983). Wet deposition is the indirect transfer of the nitrogen oxides from the atmosphere to a surface within or on a hydrometeor (e.g., rain, snow, hail, etc.), while dry deposition is the direct transfer of the compounds (gases or particulates) from the atmosphere to natural surfaces such as vegetation or soils. Conceptual and mathematical models describing these deposition processes have been developed (e.g., Droppo, 1976; Fowler, 1980).

The study of deposition processes and their associated rates and controlling factors is important for understanding the effects of nitrogen oxides on vegetation. Ambient concentrations of NOx are not the decisive factor controlling vegetation responses but rather the amount and rate of compounds absorbed by the plant. Only the absorbed pollutant is phytotoxic, not the gas phase concentration.

1.1.1.1 NOx Uptake by Plants

The deposition of gaseous nitrogen compounds to plants involves three stages: (1) transport from the atmosphere to the laminar boundary layer near the plant surface; (2) transport across the boundary layer; and (3) sorption by the plant. Stage 1 is controlled primarily by atmospheric turbulence. Stage 2 is influenced by canopy architecture and leaf shape as well as the atmospheric conditions. Stage 3 is controlled primarily by the stomata; where the resistance to mass transfer is influenced by the physiological status of the plant. The uptake of gases is frequently modeled using an analog resistance model in which the uptake is proportional to the concentration gradient between the atmosphere and the plant surfaces and inversely proportional to the resistance to gaseous transfer from the atmosphere to the leaf interior.

Studies of NOx uptake by vegetation have focused generally on uptake at the leaf or plant level (primarily stage 3) or have attempted to estimate the total deposition to the canopy. The later approach has used the deposition velocity "Vd" which is the inverse of the total resistance to transfer of gaseous NOx from the bulk air to the plant. The larger the deposition velocity, the more rapidly the gas is transferred to the plant surface. Although deposition velocity is constant for a given set of conditions and surface, the rate of deposition changes with the concentration gradient.

Reviewing earlier studies with alfalfa and oat canopies, Droppo (1976) calculated deposition velocities of 0.1, 0.5, and 2.0 cm/s for NO, NOx, and NO_2, respectively. Fowler (1980) showed that the deposition velocity for NO_2 varied with plant height, ranging between 0.1 and 0.5 cm/s and was highest when the plant had open stomata and lowest for senescent vegetation. Using eddy-correlation measurements, Wesely et al. (1982) showed that the deposition velocity of NO_2 to a soybean canopy was higher (0.6 cm/s) in the daylight than at night (0.05 cm/s). The deposition velocity for O_3 was approximately 30% larger than that for NO_2.

The deposition velocity of NO_2 to Scots pine was estimated at 0.11 and 0.02 cm/s under field and laboratory conditions, respectively (Bengston et al., 1980). The large difference between the field and laboratory estimates deserves further study. In laboratory studies, the deposition velocity of NO to Scots pine was estimated at 0.007 cm/s (Bengston et al., 1980). Another report estimated typical deposition velocities for NO_2 to a Swedish pine forest during summer day-time conditions as 0.4 to 0.8 cm/s (Grennfelt et al., 1983). Deposition velocities of NO_2 onto Populus nigra and Betula pendula have been measured at 0.287 and 0.318 cm/s (at a concentration of 0.6 ppm), respectively (Freer-Smith, 1983). For a Swedish forest ecosystem, Grennfelt et al. (1983)

estimated that the dry deposition of NOx contributed 0.4 to 1.2 kg N/ha/yr while the contribution from wet deposition was approximately 3-5 kg N/ha/yr. Although they did not determine the impact of the additional N, it could significantly influence plant growth in a N limited system.

The dry deposition of HNO_3 has received little study. Soderlund (1981) reported a deposition velocity of 1.0 cm/s for HNO_3 to a forest. In pasture conditions the deposition velocity was found to increase during the morning to a maximum near noon and then steadily decrease into the evening (Huebert, 1983). The average deposition velocity was 2.9 cm/s which is higher than the values reported for NOx. For a central Illinois grassland, the dry deposition of about 1.5 Kg HNO_3/ha month was approximately the same as that delivered by wet deposition (Huebert, 1983). In the grassland study, the dry deposition of HNO_3 contributed more N to the ecosystem than did the dry deposition of NO_2 to a forest ecosystem (Grennfelt et al., 1983). The deposition of HNO_3 into ecosystems and its possible impact is an area needing additional study.

In laboratory studies, the uptake rate of NO_2 was determined for corn, soybean, loblolly pine, and white oak to be 35, 51, 51, and 11 ng/dm^2 min pphm, respectively (Rogers, 1975). For beans, the uptake rate was estimated at 8700 ng/dm^2 min pphm (Fuhrer and Erismann, 1980), while in Scots pine, the NO_2 uptake rate was estimated to be 0.05 to 0.12 ug/m^2 s over the concentration range of 0.05 to 0.10 ppm (Bengston et al., 1980). In sweet pepper, the uptake rate of NO_2 varied between 1.5 and 3.5 ug/m^2 s over the concentration range of 0.7 to 2.0 ppm (Law and Mansfield, 1982). In sunflower, foliar injury developed when the summed NO_2 uptake for 60 minutes exceeded 12 ug/cm^2 (Omasa et al., 1981). The reason for the large differences in uptake rates among studies is unclear; it may be related to differences in experimental methods or the

experimental species. Also, several of the studies used abnormally high concentrations.

The contribution of the absorbed N from NO_2 to the plant nitrogen balance has been estimated in several studies using $^{15}NO_2$. In plants that were continuously exposed to NO_2 (0.03 ppm for 2 weeks), the absorption rate of N was estimated at 0.8 mg N/g dry weight day for tomato and sunflower but only 0.3 mg N/g dry weight day for corn (Matsumaru et al., 1979). The absorption rate for three rice cultivars and wheat was approximately 0.3 mg N/g dry weight/day and 0.45 mg N/g dry weight/day for barley (Matsumaru et al., 1981). Comparing the uptake rate among six species, corn absorbed N from NO_2 at a rate of 14 ug N/g dry weight/hr in the light, while the uptake rate ranged from 30 to 63 ug N/g dry weight/hr for 6 other species (Yoneyama et al., 1980a). Based on the above studies and the one by Rogers (1975) it appears that corn and grains are less efficient absorbers of NO_2 than are most broad leaf species.

The uptake rate of NO_2 was 10 to 20 times greater than the uptake rate for NO in several plant species (Hill, 1971; Bennett and Hill, 1973a). However, in Scots pine the NO_2 uptake rate was only three times greater than that for NO (Bengston et al., 1980).

The uptake of nitrogen oxides is proportional to the chemical potential difference (usually estimated as a concentration gradient) between the atmosphere and the leaf interior. Several studies have shown that the uptake rate increases with the atmospheric concentrations of the nitrogen oxides (Hill, 1971; Bengston et al., 1980; Rogers, 1975; Omasa et al., 1980; Srivastava et al., 1975a). In beans the uptake rate was reported to decrease with exposure time (Srivastava et al., 1975a) but this decrease was not observed in Scots pine needles (Grennfelt et al., 1983). Most studies showed that uptake was controlled by stomatal resistance; however, Srivastava et al. (1975a) reported

that a mesophyll resistance also controlled uptake. The flux of NO_2 changed with light intensity in the flacca tomato, a variety in which the stomata are open equally in the light and dark, although the transpiration rate was essentially constant (Murray, 1984). Murray concluded that the mechanism of ion transport in leaves was an important factor controlling NO_2 uptake.

In sunflowers, NO_2 uptake was proportional to the transpiration rate (Omasa et al., 1980). Bennett and Hill (1973b) observed that a higher proportion of the NOx was absorbed near the top of the plant canopy, where light intensity and metabolic rates were higher, than within the canopy. Data from several species showed that the NO_2 uptake rate varied diurnally, being 50 to 85% less in the dark than in the light (Srivastava et al., 1975a; Grennfelt et al., 1983; Yoneyama et al., 1980a; Murray, 1984). Factors that promote stomatal opening, such as high relative humidity or low CO_2, increase NO_2 uptake (Srivastava et al., 1975b). Increasing the salinity in the soil solution decreased NO_2 uptake (Fuhrer and Erismann, 1980).

The observations that the N content of plants exposed to NO_2 increased support the fact that plants can absorb NO_2 and utilize it metabolically. For example, Faller (1972) showed that sunflowers grown in the absence of N in the soil solution could use atmospheric NO_2 as the sole N source. Plant growth and N content increased in relation to the NO_2 concentration in the air.

1.1.1.2 NOx Uptake by Soils

The dry deposition of gases to soils provides another route, in addition to vegetation, for nitrogen oxides entrance into the ecosystem. Limited laboratory studies have measured NOx uptake by soils. In these studies, soils were placed in sealed containers and either NO or NO_2 was injected; the gas phase and soil concentrations of N were monitored over time. Within 10 to 15

minutes, air-dry calcareous soils absorbed 0.5 to 2% NO by weight from dry air containing 1.6% NO by volume (Prather et al., 1974). Less than 10% of the absorbed NO was desorbed when the soil was heated to 105 C or exposed to a low pressure for 24 hr. The uptake of NO increased with moisture content of the soil and/or air and the absorbed NO was recovered as nitrate (Miyamoto et al., 1974). Studies with sterile and nonsterile loamy soils exposed to 10 to 25 ul/l NO_2 showed that they absorbed more than 99% of the gas within 10 to 15 min (Ghiorse and Alexander, 1976). Within the soil, the NO_2 was converted into both nitrite and nitrate. Data from Smith and Mayfield (1978) showed similar uptake percentages and conversion products within the soil. Nitrogen dioxide absorbed by soils is available to the plant for uptake (Yoneyama et al., 1980b). The authors concluded that plants could absorb a considerable amount of N, via the soil absorption of NO_2, when the plants were fumigated with NO_2 for extended time periods. However, these studies all used NO and NO_2 concentrations much greater than occur in the ambient air. The dry deposition of HNO_3 to soils has received only limited study; however, the deposition velocities for HNO_3 are apparently similar to those for SO_2 and range from 3 to 10 mm/s (Fowler, 1980). The limited studies indicate that soils can be an important sink for NOx and HNO_3, but the biological significance of the uptake is not known.

1.1.1.3 Reactions That May Scavenge NOx Within Cells

The diffusion of NOx from extracellular deposition sites to perturbation sites within the cells includes movement through an aqueous phase. Along this pathway the compounds may experience diffusion and/or bulk flow through the hydrated cells, membranes and cytosol, each of which is more viscous than air. Consequently, diffusion is slower in the aqueous phase than in air. Within the

aqueous phase, hydrated nitrogen oxides may undergo reactions which reduce the amount of hydrated oxides reaching cellular perturbation sites.

Within the leaf, nitrogen oxides dissolve in the water on the cell surfaces. Nitrogen dioxide is highly soluble in water where it forms nitrate and nitrite which can be oxidized to nitrate in an oxidizing environment. Nitric oxide is less soluble in water than NO_2 and this lower solubility is frequently given as the reason for its lower uptake rate and toxicity. However, Anderson and Mansfield (1979) found that NO was more soluble in xylem sap, which is continuous with the extracellular water in a leaf, than in distilled water. This suggests that NO may be absorbed at a higher rate than expected based on its aqueous solubility.

Plants have metabolic paths by which they can metabolize (reduce) hydrated nitrogen oxides to ammonia which is incorporated into organic substances. The nitrate and nitrite formed by the solvation of NOx can be reduced by nitrate reductase (localized within the cytoplasm) and by nitrite reductase (localized within the chloroplast). The enzyme nitrate reductase is induced by its substrate nitrate and utilizes reductant formed during respiration; whereas, nitrite reductase utilizes reduced ferredoxin produced in photosynthesis to reduce nitrite to ammonia.

Pea plants exposed to high concentrations of NO_2 accumulated nitrate and nitrite, which increased with exposure concentration and duration (Zeevaart, 1976). Nitrate accumulated in beans in proportion to the NO_2 exposure but nitrite did not accumulate (Srivastava and Ormrod, 1984). Spinach and sunflower exposed to NO_2 in the light transformed 99% of the absorbed N into reduced N-compounds (Kaji et al., 1980). While in the dark only 85% of the absorbed N was reduced; the unreduced N was in the form of nitrate and nitrite. The reduced nitrogen was incorporated primarily into amides and amino acids.

Other studies support the observations that the absorbed NO_2 is converted into nitrate and nitrite which is subsequently metabolized (Yoneyama and Sasakawa, 1979; Yoneyama et al., 1979).

Exposure of pea seedlings to high concentrations of NO_2 induced nitrate reductase activity (Zeevaart, 1974). Studies with beans showed that low concentrations of NO_2 (0.02 or 0.10 ppm for 5 days) increased nitrate reductase activity, probably a consequence of the increased tissue nitrate concentration (Srivastava and Ormrod, 1984). Nitrogen dioxide exposure also increased the rate of nitrite reductase, with the rate of increase varying among species (Yoneyama et al., 1979), while nitrite reductase also increased in tomatoes exposed to NO (Wellburn et al., 1980). The increases in enzyme activity is indirect evidence that NO_2 and NO fumigations increase nitrate and nitrite levels in plant tissue.

Fumigation with a high concentration of NO_2 (4 ppm) increased the content of amino groups and protein in several plant species (Zeevaart, 1976). Using N-15 labeled nitrogen dioxide, several research groups have shown that the absorbed NO_2 is reduced and converted into reduced nitrogen compounds (Durmishidze and Nutsubidze, 1976; Yoneyama and Sasakawa, 1979; Rogers et al., 1979) and translocated throughout the plant.

The available data indicate a role for nitrate and nitrite reduction in the metabolism and a probable detoxification of the NOx absorbed by plants. Volatilization of NO has been observed from plant tissue treated with herbicides (Klepper, 1979) and during *in vivo* assays for nitrate reductase (Harper, 1981). The release of NO was associated with an accumulation of nitrite. This path may also provide a pathway for plants to detoxify NOx.

1.1.2 Perturbation

Perturbation is the initial phytotoxic event which results from NOx-induced alterations in cellular structure or function. At present, the site of NO toxicity is unresolved. Hill and Bennett (1970) proposed that the toxicity of NO resulted from its interaction with ferredoxin. However, Wellburn et al. (1980) questioned this proposal since NO must pass through several membranes to come in contact with the ferredoxin in the chloroplast.

Nitrogen dioxide is a reactive molecule and reactions with biological membranes have been proposed (Mudd et al., 1984; Rowlands et al., 1977) as the possible site of perturbation. But, within plant cells, there is no evidence of NO_2 reactions with the plasma membrane (Mudd et al., 1984). Most evidence indicates that the NO_2 effects are the consequences of elevated nitrate and nitrite levels within the cells. However, lack of information on the concentrations of these ions in cellular compartments limits our understanding of the initial phytotoxic events.

Most plants can tolerate an accumulation of nitrate, although elevated concentrations in the food web may be undesirable. Several lines of evidence suggest that the nitrite ion is the toxic species, but it is not clear if the toxicity results from an accumulation of the ion or acidification reactions. In several species, foliar injury has been correlated with nitrite accumulation (Zeevaart, 1976; Kato et al., 1974; Yoneyama et al., 1979). Plants exposed to NO_2 in the dark or treated with the photosynthetic inhibitor, DCMU, sustained more injury than plants exposed in the light. This response is consistent with the photoreduction of nitrite to ammonia as a detoxification reaction (Zeevaart, 1976; Kato et al., 1974; Inden 1975; Yoneyama and Sasakawa, 1979). Amundson and MacLean (1982) speculated that the sensitivity of several urban tree species to NO_2 occurred because the leaves lacked the enzymes necessary to

detoxify nitrate and nitrite. The increased sensitivity of spinach to NO_2 exposures in the dark was associated with elevated tissue nitrate concentrations as a consequence of reduced nitrite reductase activity (Hogsett et al., 1981).

Acidification of the cell sap was observed following exposure of plants to high concentrations of NO_2 suggesting that the injury was the result of a pH decrease (Zeevaart, 1976). The addition of nitrite to a thylakoid suspension decreased the light-induced pH gradient across the thylakoid membrane (Robinson and Wellburn, 1983). A pH decrease of 1 unit, which could have a significant effect on plant metabolism, was caused by the addition of 1.5 mM nitrite. Nitrite treatment (2 mmoles) caused the release of Mn from thylakoid membranes, leading Wellburn (1982) to suggest that nitrite may induce free radical reactions.

Although various studies have investigated the mode of NOx toxicity, no clear conclusion can be drawn concerning the site of action or the toxic species.

1.1.3 Homeostasis

Homeostasis is a series of processes that permit living systems to maintain themselves in a world of destructive forces. Following perturbation by an air pollutant, living cells attempt to reestablish their normal metabolic level using repair or compensatory processes (Tingey and Taylor, 1982). Because the repair or compensation may range from partial to complete, the degree of injury will vary also. Homeostatic processes have not been studied in relation to NOx, however, their presence can be inferred by analogy with other pollutants. One of the first visible indications of NO_2 injury is the appearance of water-soaked (shiny or oily) areas on the leaf surface caused by water leaking from the surrounding cells into the intercellular spaces. If the

tissue is not irreversibly injured, the water-soaking is temporary; not all areas that initially display water-soaking ultimately develop necrosis, an indication of homeostatic processes.

1.1.4 Injury

Injury results from the inability of the organism to repair or compensate for the perturbation. Biochemically and physiologically, injury is expressed as alterations in cellular function and metabolism, including changes in enzyme activity and metabolic pools. These changes may, in part, result from changes in the structure of cellular components. Most of the changes in cellular structure and metabolism observed in plants exposed to nitrogen oxides are the result of the perturbation, not the cause of it. Visible injury is the consequence of altered cellular processes. Alterations of cellular processes also cause changes in carbohydrate allocation, plant growth and yield.

1.1.4.1 Ultrastructural Changes

Ultrastructural changes induced by NO_2 have been studied in several species, but generally the concentrations used were much higher than those measured in the ambient air. Following NO_2 fumigation the plasma membrane appeared normal, as did other cellular membranes (Matsushima et al., 1977); however, there was an increased frequency of invaginations in chloroplasts and mitochondria (Dolzmann and Ullrich, 1966; Lopata and Ullrich, 1975). Fibrillar and crystalloid structures were observed in the chloroplast stroma following NO_2 exposure (Dolzmann and Ullrich, 1966; Lopata and Ullrich, 1975). Thylakoid swelling results from NO_2 exposure (Wellburn et al., 1972), however, other pollutants also induce swelling suggesting, that if it is a general symptom of acute injury rather than a specific indicator of NO_2. The limited results from

ultrastructural studies suggest that the primary effects of NO_2 are on the chloroplast and not on the plasma membrane.

1.1.4.2 Effects on Photosynthesis, Respiration, Gas Exchange

Both NO_2 and NO have been shown to suppress photosynthesis, frequently at concentrations and exposure durations that induce no visible injury. The magnitude of photosynthetic inhibition increased with the NO_2 concentration and exposure duration (Hill and Bennett, 1970; Srivastava et al., 1975a). Most of the inhibitory effect occurred within an hour after the start of the exposure, but photosynthesis continued to decline at a slow rate as long as the exposure continued. For alfalfa and oats, threshold concentrations that inhibited photosynthesis were estimated to be 0.5 to 0.7 ppm NO_2 for 45 to 90 minutes. The inhibition of photosynthesis was not permanent (Hill and Bennett, 1970); recovery started immediately after the exposure terminated, with the time to full recovery depending on the magnitude of inhibition. Nitrogen dioxide concentrations of 1.0 ppm or greater for 0.5 hr or longer significantly depressed photosynthesis in beans (Srivastava et al., 1975a). The percent inhibition changed with leaf age, being the largest for the leaves that had the highest photosynthetic rates. Similarly, NO_2 effects were the greatest under high light, high relative humidity and optimum temperature for photosynthesis (Srivastava et al., 1975b). Sunflower photosynthesis was not inhibited by 1.0 ppm NO_2 for 1 hr, nor was the photosynthetic rate of rice or corn reduced by 0.5 to 5.0 ppm NO_2 for 1 hr (Furukawa and Totsuka, 1979; Taniyama, 1979). However, 10 ppm for 1 hr reduced photosynthesis by 60%. Over a 20-hr period, 0.25 and 0.50 ppm NO_2 inhibited photosynthesis in tomatoes 31 and 32%, respectively (Capron and Mansfield, 1976).

Hill and Bennett (1970) reported that NO was about half as effective in reducing photosynthesis in oats and alfalfa as NO_2. However, NO caused a faster decrease in the photosynthetic rate but it also recovered faster in plants exposed to NO in with plants exposed to NO_2. The recovery from NO exposure was frequently complete within 1 hr. In tomato, NO was approximately as effective in reducing photosynthesis as NO_2 (Capron and Mansfield, 1976). The combined effects of NO_2 and NO from simultaneous exposures, on photosynthesis were approximately additive (Hill and Bennett, 1970; Capron and Mansfield, 1976).

Nitrogen dioxide reduced photosynthesis to a greater extent than transpiration or stomatal conductance (Hill and Bennett, 1970; Srivastava et al., 1975a,b), indicating that the inhibitory effect of NO_2 on photosynthesis occurred within the leaf and not at the level of CO_2 diffusion into the leaf. Most data suggest that NO_2 exposures stimulate the activity of RuBP carboxylase, the enzyme that catalyzes CO_2 reduction during photosynthesis. Pea plants were exposed to 0.1 or 1.0 ppm NO_2 for 6 days (Horsman and Wellburn, 1975); the low concentration had no effect on RuBP carboxylase activity while the the high concentration (1.0 ppm) stimulated enzyme acitivity 7%. In Jack pine and white spruce, NO_2 (0.2 to 1 ppm for 2 weeks) stimulated the RuBP carboxylase activity; the amount of increase depended on the NO_2 concentration (Malhotra and Khan, 1984). The stimulation also occurred in Jack pine exposed to 2.0 ppm NO_2 for 48 hr. In contrast, RuBP carboxylase activity in white birch and American green alder was inhibited even at an NO_2 concentration of 0.2 ppm (Malhotra and Khan, 1984). Although NO_2 may inhibit photosynthesis, its effects on RuBP carboxylase suggest that enzyme inactivation is not the primary site of the inhibition.

In several grass species, NO_2 (0.11 ppm for 103.5 hr/week for 20 weeks) stimulated ATP formation (Wellburn, 1982). Dark respiration of bean leaves was inhibited to a greater extent than photosynthesis by increasing NO_2 concentrations and did not recover as readily following the termination of the exposure (Srivastava et al., 1975b). The rate of CO_2 evolution into CO_2 free-air (a measure of photorespiration) was also inhibited.

Both NO_2 and NOx have been shown to decrease photosynthesis, dark respiration, photorespiration and transpiration rates in several plant species. However, these effects have been observed at concentrations well in excess of those that occur in the ambient air, except around a few emission sources.

1.1.4.3 Effects on Metabolism

Only a few studies have considered the effects of nitrogen oxides on plant metabolism. Except for studies concerning the effects of NOx on nitrogen metabolism the data are limited to reports on isolated facets of metabolism.

Short-term exposures of NO and NO_2 have been shown to stimulate nitrate and nitrite reductase activity (see section 1.1.1.3). However, in plants exposed to 0.4 ppm NO for 28 days, nitrate reductase activity decreased and nitrite reductase acitivity was stimulated (Wellburn et al., 1980). In plants, ammonia is the end product of nitrate and nitrite reduction via nitrate and nitrite reductases. The accepted mode of ammonia incorporation into amino acids is via the glutamine synthetase/glutamate synthase pathway rather than via glutamate dehydrogenase (Wellburn, 1982). Nitrogen dioxide caused a slight increase in glutamine synthetase but had no effect on glutamate dehydrogenase in peas (1 or 2 ppm for 6 days) or rye grass (0.25 ppm for 63 days) (Wellburn, 1982). In beans, glutamine synthase was stimulated and glutamate dehydrogenase decreased following NO_2 exposure (0.02 to 0.50 ppm for 5 days) (Srivastava and

Ormrod, 1984). In a NO-sensitive tomato cultivar, NO (0.4 ppm for 2 weeks) stimulated glutamate dehydrogenase (reductive amination), glutamate oxaloacetate transaminase and glutamate pyruvate transaminase activities to higher levels than in a less sensitive cultivar (Wellburn et al., 1980). Although the enzymes of nitrogen assimilation were stimulated there was not a significant change in the protein content over the 28-day exposure period.

Horsman and Wellburn (1975) investigated the effects of NO_2 on several enzymes in pea foliage. The plants were exposed to 0 or 1.0 ppm NO_2 for 14 days and the enzyme activity was determined. The RuBP carboxylase activity was increased 7% but there were no significant changes in the activities of the following enzymes: peroxidase, glutamate pyruvate transaminase, or glutamate oxaloacetate transaminase. Peroxidase was stimulated by NO_2 (2.0 ppm for 48 hr) in Jack pine, while in American green alder the activity was stimulated by 0.2 ppm for 24 hr (Malhotra and Khan, 1984). Nitrogen dioxide (18 ppm for 2 hr) increased the foliar concentration of the isoflavoniod, coumestrol, about 10-fold above the control level in soybean foliage but did not elicit the formation of hydroxphaseollin (Keen and Taylor, 1975). Although considerable foliar injury occurred, the rate of isoflavoniod accumulation was substantially less than for soybeans treated with ozone. In Jack pine, NO_2 (2 ppm for 48 hr) inhibited the biosynthesis of phospholipids and galactolipids (Malhotra and Khan, 1984).

The effects of nitrogen oxides on plant pigments display two different types of response. In leaf tissue that displayed visible injury, the chlorophyll concentration was decreased and phaeophytin a was formed (Kandler and Ullrich, 1964); the content of carotene was also decreased. However, the pigments were normal in uninjured tissue. Increased chlorophyll concentrations have been reported in several plant species exposed to elevated NO_2 concentra-

tions for extented time periods (Taylor and Eaton, 1966; Horsman and Wellburn, 1975). Nitric oxide can also increase chlorophyll concentrations (Wellburn et al., 1980).

1.1.5 Effects of NOx on Plant Communities and Ecosystems

Ecosystems are complex self-sustaining systems composed of living organisms and their environment. The system includes the various organismal/-environmental interactions that couple the living and non-living components into a stable system. It is difficult to determine the consequence of a given pollutant exposure on a single plant and the problems are magnified when the impact of a pollutant on a plant community or ecosystem must be assessed. The response of a community or ecosystem to an environmental perturbation is determined by the responses of their constituent organisms. However, the response of the individual organisms can not be summed to predict the response of the system, because of non-linear interactions among the various components. For example, studies on pure and mixed stands of ryegrass, hairy vetch and crimson clover showed that SO_2-induced changes in the composition of the plant communities were not totally explained by the direct effect of the SO_2 on the differentially susceptible species (Guderian, 1966). Under the influence of SO_2, there were changes in interspecific competition. The primary impact on the more susceptible members of the stand was so increased that they could no longer compete effectively for the required growth factors (mineral nutrients, water, light, growing space) and consequently they lost their importance in the community structure. As a consequence of the change in competitive conditions, the decline in the more sensitive members of the stand permitted enhanced growth for the more resistant species. The total yield was decreased less than would be expected from the loss of the susceptible species alone. Similar

results have been reported for ozone (Bennett and Runeckles, 1977; Montes et al., 1982).

Studies of the effects of nitrogen oxides on agricultural and native vegetation showed that species differed in their sensitivity. Differences in sensitivity were ascribed to climatic, edaphic and phenological stages. However, there is little known about the specific effects of nitrogen oxides on natural plant communites. Effects on growth and visible injury have been observed only around specific NOx emitters. Effects were observed on Scots pine in the vicinity of a fertilizer plant in Poland that emitted mainly nitrogen compounds, i.e., particulate nitrate, gaseous ammonia and nitrogen oxides (Kawecka, 1973). At this site the exposure was very intense; the annual deposition of N was 1000 to 1200 kg/ha. All the trees within 1 km of the source were killed and serious injury extended for another kilometer. Studies in the vicinity of an arsenal found foliar injury on several coniferous species which was attributed to NOx or the interaction of NOx and SO_2 (Skelly et al., 1972). Subsequent studies showed that the growth rates of white pine and tulip poplar were correlated with emissions over a 30 year period (Stone and Skelly, 1974). Growth reductions were detected in both trees displaying injury symptoms and those that did not (Phillips et al., 1977). Although impacts of nitrogen oxides on plant communities have been reported, it is difficult to extrapolate these results to other communities because the effects were the consequence of significantly more intense exposures than are typically found in natural plant communities.

The dry and wet deposition of nitrogen compounds into an ecosystem may have significant impacts on the system. Predicting the effects of these depositions on ecosystems involves greater uncertainty than estimating the impacts on an agricultural crop. In the United States, the atmospheric

contributions of nitrate can range from less than 0.1 kg N/ha year in the Northwest to almost 5 kg N/ha/yr in the Northeast (U.S. EPA, 1982). Total atmospheric deposition of nitrogen commonly ranges from about 10 to 20 kg N/ha/yr year for most of the United States (U.S. EPA, 1982). By comparison, Grennfelt et al. (1983) estimated the dry deposition of NOx to a Swedish forest at up to 1.2 kg N/ha/yr and the total N deposition at 3 to 5 kg N/ha/yr. In some ecosystems occult precipitation, which is not efficiently collected in rain gauges as wet deposition, can be a significant route of N input to the system (Dollard et al., 1983). For the United States, total nitrogen in bulk precipitation represents about 8 to 25% of the annual plant needs in eastern deciduous and western coniferous forest ecosystems (U.S. EPA, 1982). Although these data suggest that plant growth in terrestrial ecosystems is influenced by the atmospheric input of N, it is not yet possible to estimate the importance of these contributions (U.S. EPA, 1982). However, in nitrogen deficient ecosystems such atmospheric inputs are likely to increase biological productivity.

1.1.6 Effects of NOx on Lower Plants and Microorganisms

Only a few studies have investigated the effects of nitrogen oxides on lower plants and microorganisms. Higher plants have been the focus of most studies, primarily because of economic considerations. At the cellular level it is assumed that the mode of action is similar for both higher and lower plants. However, differences in morphology and anatomy may have a significant influence on the rate of pollutant uptake. Thallophytes, which lack cuticles and most other protective tissue, may display a high uptake rate when the thalli are hydrated. However, based on the limited studies it is not possible to conclude that this renders lower plants more susceptible than higher plants.

Alexander et al. (1977) reviewed the effects of NOx on microorganisms and concluded that knowledge concerning the potential impact of NOx on microbial processes in soils and waters is sparse. Most of the experimental studies used unrealistic concentrations and/or exposure conditions. Therefore, although it is not likely that ambient concentrations of NOx significantly affect biological processes in ecosystems, it is not possible to support this view with data. In more recent studies, the rate of glucose decomposition in an acid forest soil was not reduced following exposure to 1 ppm NO_2 for 13 days, while an exposure to 10 ppm for 6 days reduced the rate only 13% (Grant et al., 1979). The photosynthetic rate of the blue-green algae Anabaena in an acid soil (pH 4.9) was almost totally inhibited following exposure to 5 ppm NO_2 for 3 days (Wodzinski and Alexander, 1980). But in a soil suspension at pH 6.0, 15 ppm NO_2 for 3 days reduced photosynthesis only 15%. The photosynthetic rate of green algae in an acid soil (pH 4.2) was not impacted by 15 ppm for 3 days (Wodzinski and Alexander, 1980).

Four lichen species were exposed to NO_2 (1 to 8 ppm) for 6 hr and the chlorophyll content was used to determine the effect (Nash, 1976). Significant chlorophyll reductions were found in each of the species following exposure to 4 or 8 ppm NO_2. Nash (1976) concluded that NO_2 was probably a relatively insignificant phytotoxicant for lichens because the concentrations required to cause an effect were substantially greater than those in the ambient air. However, he recommended that future studies consider the possible synergistic effects of NO_2 and SO_2.

The above data support the conclusion that lower plants are relatively tolerant of NO_2, as are higher plants. Gas-phase concentrations required to cause effects are much higher than occur in the ambient. However, caution must be exercised concerning the possible effects of nitrate and nitrite delivered

to the plants via wet deposition processes, as thallophytes can absorb the ions directly from the environment. Nitrite (0.5 to 1.0 mM) can reduce the chlorophyll content of lichens and the photosynthetic rate of algae (Marti, 1983; Wodzinski et al., 1977). Additional studies are required to determine if the wet deposition rates that occur in ambient conditons are detrimental to lower plants.

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